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OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT: N00014-90-J-1148

R & T Code 4132016

Design, Synthesis and Characterization of Novel Nonlinear Optical Polymers

Dr. Sukant Tripathy
University of Massachusetts Lowell
Department of Chemistry
1 University Avenue
Lowell, Massachusetts 01854

May 14, 1992

OFFICE OF NAVAL RESEARCH
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R & T : 4132016

GRANT Number: **N00014-90-J-1148**

GRANT Title: **Design, Synthesis and Characterization of Novel Nonlinear Optical Polymers**

Principal Investigator: Dr. Sukant Tripathy

Mailing Address: University of Massachusetts Lowell
Department of Chemistry
1 University Avenue
Lowell, Massachusetts 01854

Part I

a. Number of papers submitted to refereed journals, but not published: 2

b. Number of papers published in refereed journals (list attached): 5

c. Number of books or chapters submitted, but not published: 1

d. Number of books or chapters published: 0

e. Number of printed technical reports & non-refereed papers (list attached): 4

f. Number of patents filed: 0

g. Number of patents granted (list attached): 1

h. Number of invited presentations at workshops or professional society meetings: 8

i. Number of presentations at workshops or professional society meetings: 6

j. Honors/Awards/Prizes for contract/grant employees (list attached): 4

k. Total number of graduate students and post-doctoral associates supported by at least 25 % during this period, under the R & T project number:

Graduate Students: 1
Post-Doctoral Associates: 2
including the number of,
Female Graduate Students: 0
Female Post-Doctoral Associates: 0
the number of,
Minority Graduate Students: 0
Minority Post-Doctoral Associates: 0
and the number of,
Asian Graduate Students: 1
Asian Post-Doctoral Associates: 2

Graduate students Mr. Ru Jong Jeng and Mr. Lian Li were supported under this R & T project number during the reported period. However, the amount of their support was less than 25 %, as the remainder of their support was provided by the University of Massachusetts Lowell through graduate research assistantships.

l. Other funding (list agency, grant title, amount received this year, total amount, and the period of performance, and briefly state the relationship of that research to your ONR grant):

Department of the Army, University Research Initiative
Intelligent Materials and Structures Based on Ordered Assemblies of DNA
co-principal investigator with Professors Kenneth Marx and Jayant Kumar
Research Grant, March 15, 1992 - March 14, 1993 - $155,000.00

University of Maryland, Baltimore
UltraHigh Speed Optical Analog-to Digital Converter
Research Grant, February 1, 1992 - January 31, 1993 - $5,000.00

Electric Power Research Institute
Evaluation of Unique Solar Energy Conversion Concept
Research Grant, October 14, 1991 - September 30, 1992 - $85,000.00

American Chemical Society/Petroleum Research Fund
Novel Photocrosslinked NLO Polymers and Related Electro-Optic Devices
Research Grant, January 1, 1992 - December 31, 1992 - $20,000.00

The research listed above is not related to the reported ONR grant.

Part II

a. Principal Investigator: Dr. Sukant Tripathy

b. Current telephone number: 508-458-7116

c. Cognizant Scientific Officer: Dr. JoAnn Milliken

d. Brief description of the project.

The principal focus of the project is to develop new materials chemistry based on molecular level design and solid state chemistry. The goals have been to develop electroactive polymers with novel electronic, optical and nonlinear optical properties. Second and third order nonlinear optical materials have been developed based on conjugated macromolecules and asymmetric anharmonic molecular electronic dipolar oscillators.

In this multidisciplinary research effort, starting from first principle, polymeric systems have been developed with stable large nonlinear optical coefficients, ultrathin electroactive redox monolayers, molecular superlattices etc. Photochemical crosslinking and photopolymerization have been employed as engineering tools in materials fabrication and to elicit new phenomenon.

e. Significant results during last year.

1. A new class of stable (temporal and thermal) second order nonlinear optical materials has been developed based on sol-gel chemistry.

2. Suitable design of the NLO chromophore has led to some of the largest photoconductivities in these polymers without the addition of charge transporters or dye sensitizers. Large photoconductivity, small dark conductivity, stable and large electrooptic coefficients make this class, efficient candidate photorefractive materials.

3. Poling and crosslinking has led to the observation of photovoltage in these polymers. Conducting polythiophene has been used as one of the host matrices.

4. Efficient Cerenkov Second Harmonic Generation in guided wave structures has been demonstrated using a number of candidate crosslinkable NLO polymers.

f. Brief summary of plans for next years work.

Design: Molecular units with transparency to shorter wavelengths, larger dipole moment, stabler holes and large figure of merit for photorefractive effects will be designed.

Dynamics simulation of these systems will be carried out to study molecular motion, packing and orientational stability. Electronic and optical properties will be estimated. A model for photovoltaic effect will be developed.

Synthesis: Above designed molecular units appropriately functionalized will be synthesized. These molecular units will be incorporated into macromolecular architecture as side chains, in the main chain and in other articulated structures. Photochemistry in thin films, in monolayers (L-B) and under orientation fields will be carried out.

Processing: Mono and multilayers and spun on films will be fabricated. Chemistry will be carried out in these films under applied fields. Microfabrication and direct processing will be carried out using the photocrosslinkability by using photomasks and direct laser beam writing.

Characterization: Details of the photochemical reactions will be investigated using numerous solid state in situ characterization techniques. Polarized FT-IR, FT-Raman, UV-Vis-Near IR spectroscopies will be carried out as a function of photoprocessing and field induced modifications. Other linear and nonlinear optical properties will be investigated. Dynamic mechanical analysis, dielectric measurements and thermal analysis will be carried out to study molecular motion organization and property aspects. Photoconductivity and photovoltage will be measured.

g. Name of graduate students and post-doctorals currently working on the project.

Post-doctorals

Dr. Manjunath Kamath Bola and Dr. NagendraBabu Kodali

Graduate students (Ph.D. Candidates)	*Department*
Mr. Govindasamy Chittibabu	Chemistry
Mr. Yong Ming Chen	Physics
Mr. Ru Jong Jeng	Chemistry
Mr. Lian Li	Physics
Ms. Sutiyao Marturunkakul	Chemistry
Undergraduate students	*Department*
Mr. Craig Masse	Chemistry

Part III

Research Highlights

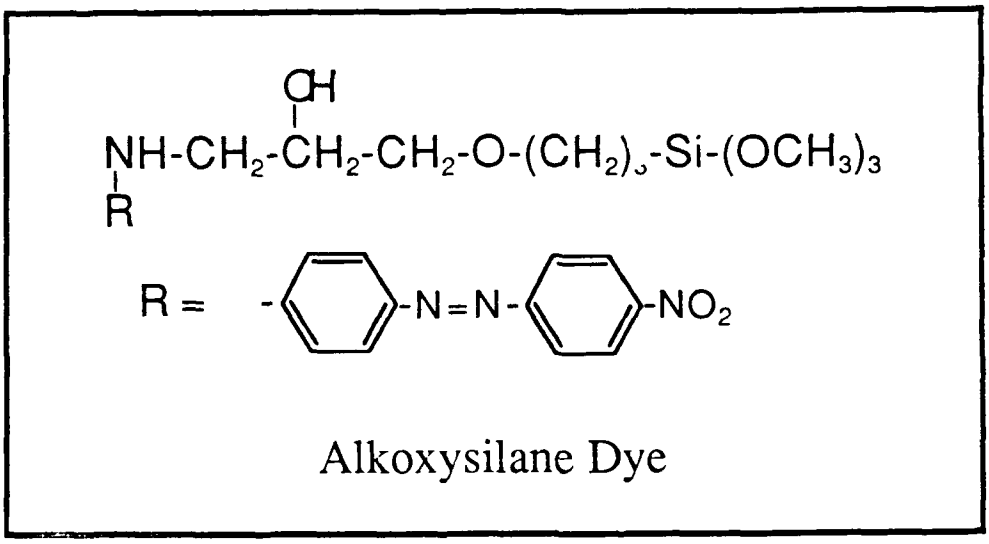
Problem:

Development of stable poled nonlinear optical (NLO) polymers for second order processes.

Approach:

Guest-Host system of an alkoxysilane NLO dye and phenyl siloxane oligomers can be poled and vitrified by curing at high temperature (200 °C). The resultant NLO glass is stable at elevated temperatures. It retains 55 % of the original d_{33} value after heating at 100 °C for 40 hours.

The dye used is shown below.



Alkoxysilane Dye

The spin on siloxane used is shown below.

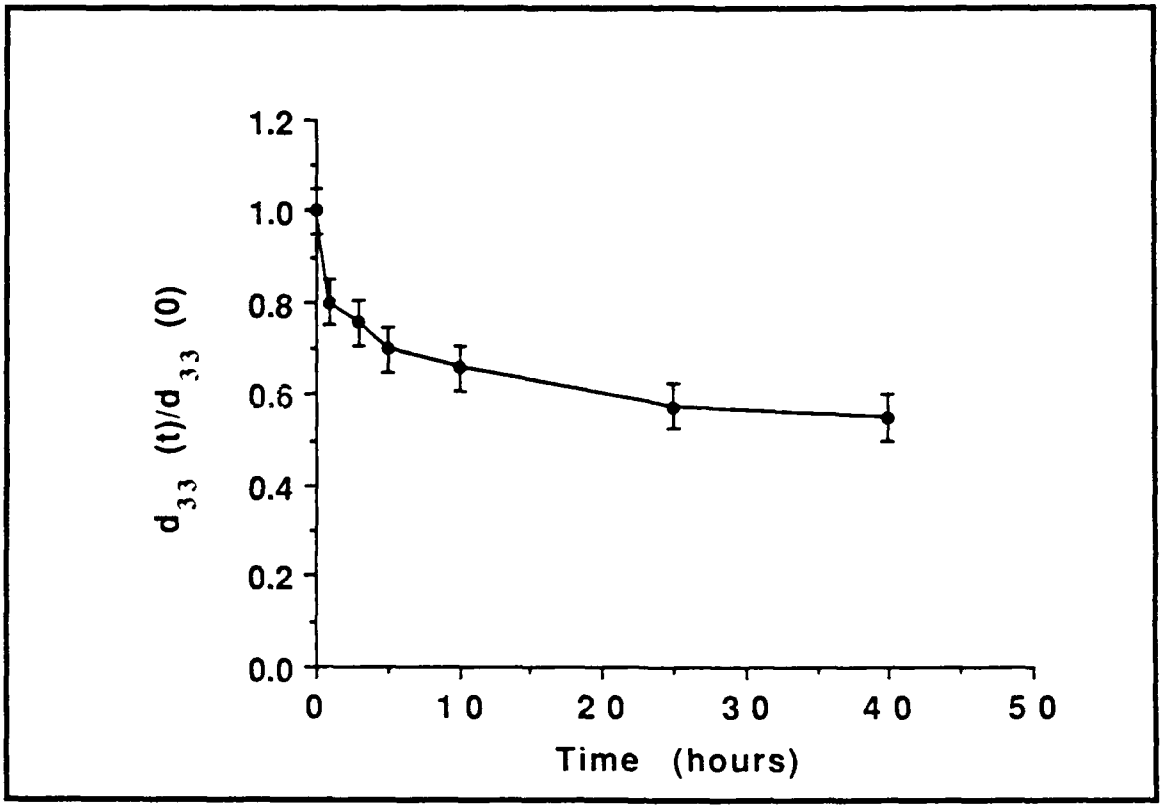
$$[(SiO)_a(C_6H_5)_b(OC_2H_5)_c(OH)_d]_n$$

$$a \geq 1$$

$$b,\ c,\ d \leq 0.5$$

$$n = 5 - 100$$

The silane dye can be crosslinked into polyamic acid systems as well.



Summary:

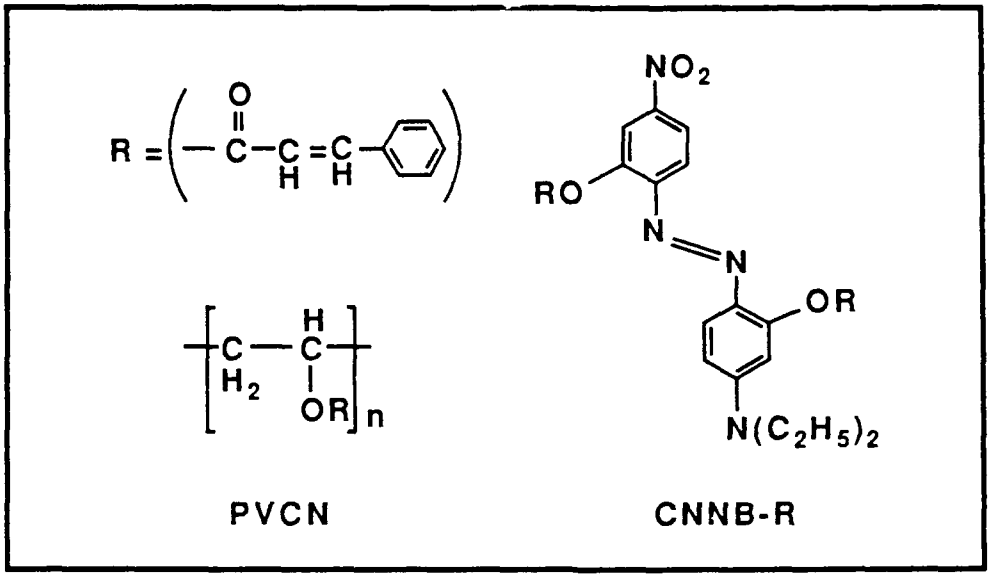
Stable NLO second order materials may be produced via the sol-gel route. The stability of the poled order is dictated by the curing temperature. The degradation temperature of the dye is thus the limiting factor in the stability of this class of materials.

Problem:

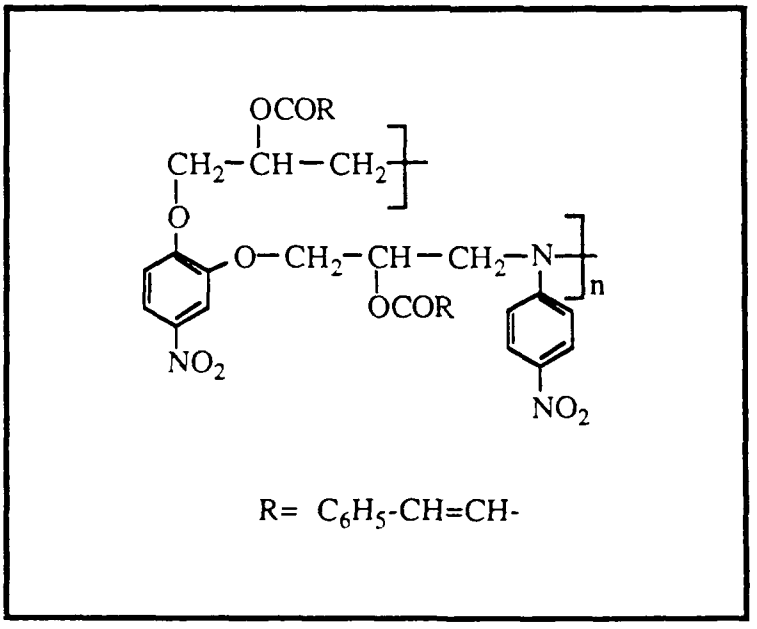
Photoconductivity in single component electro-optic polymers.

Approach:

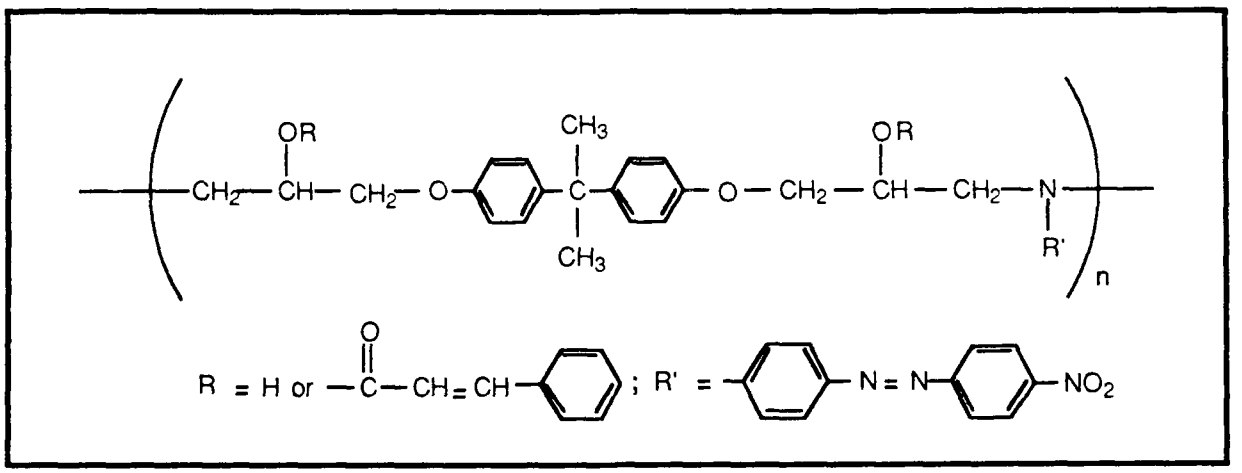
Several classes of photocrosslinkable NLO polymers have been developed. A tertiary amine acts as a stable hole in these systems upon photocarrier generation via the NLO dye. Substantial photocurrent has been measured in these systems. Photovoltage has also been demonstrated in the poled films. There are no charges in the system to provide dark conduction.



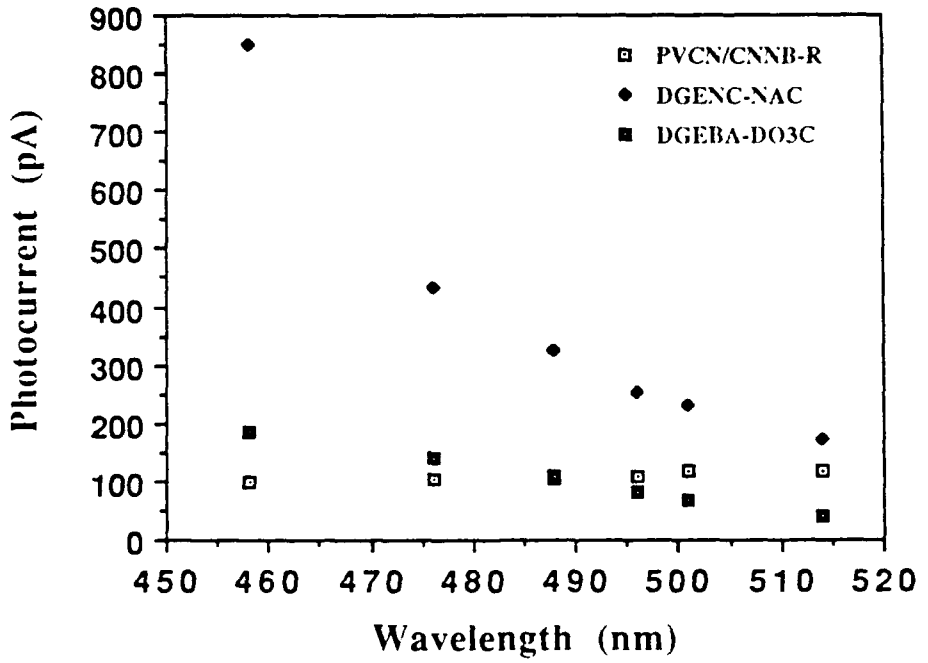
Chemical structures of the host – PVCN (polyvinylcinnamate) and the guest–(CNNB-R)(3-cinnamoyloxy-4-[4-(N,N-diethylamino)-2-cinnamoyloxy phenylazo] nitrobenzene)



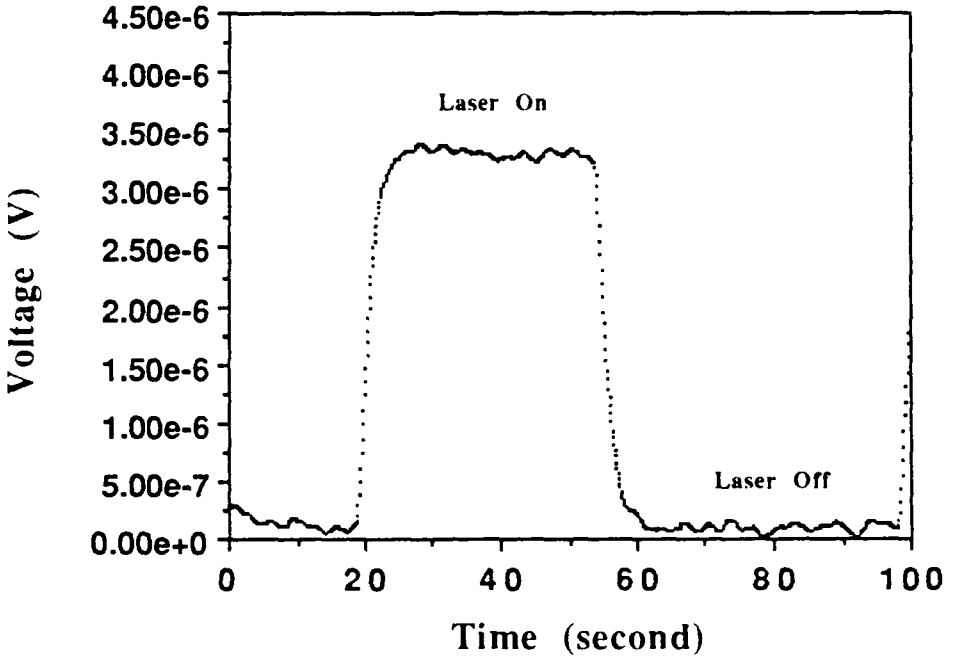
Chemical structure of the epoxy-based polymer DGENC-NAC(diglycidyl ether nitrocatechol/nitroaniline prepolymer functionalized with cinnamoyl groups)



Chemical structure of DGEBA–DO3C (diglycidyl ether of bisphenol A and 4 [4'-nitrophenylazo] phenylamine [Disperse Orange 3])



Spectral dependence of photocurrent measured for the three NLO polymers.



Photovoltage measured for the sample with the planar gap geometry at $\lambda = 514$ nm with 100 mW laser power.

Summary:

Photovoltage generation in the poled polymers is an exciting new phenomenon. Poled crosslinked electro-optic polymers show significant photoconduction to be candidate materials for single component photorefractives.

b. Number of papers published in refereed journals (list attached): **5**

1. "Third-Order Optical Nonlinearities in a Photocrosslinkable Polymer," L. Li, J.Y. Lee, X.F. Zhu, J. Kumar and S.K. Tripathy, Japn. J. Appl. Phys. 31 (1992).

2. "Photoconductivity in a Photocrosslinkable Second Order Nonlinear Optical Polymer," (L. Li, J.Y. Lee, Y. Yang, J. Kumar and S. Tripathy), Applied Physics B 53 279 (1992).

3. "New Photocrosslinkable Polymers for Second Order Nonlinear Optical Processes," (B.K. Mandal, R.J. Jeng, J. Kumar and S. Tripathy), Makromol. Chem., Rapid Commun. 12 (1991).

4. "A New Guest-Host System: Towards Stable Second-Order Optical Nonlinearity," (R.J. Jeng, Y.M. Chen, A.K. Jain, S.K. Tripathy and J. Kumar), Optics Communications 89 212 (1992).

5. "Photocrosslinkable Polymers with Stable Second Order Optical Nonlinearity," (X.F. Zhu, Y.M. Chen, L. Li, R.J. Jeng, B.K. Mandal, J. Kumar and S.K. Tripathy), Optics Communication 88 77 (1992).

e. Number of printed technical reports & non-refereed papers (list attached): **4**

1. "Photoprocessable Second Order Nonlinear Optical Polymers," (J. Kumar, S.K. Tripathy, B.K. Mandal, Y.M. Chen and R.J. Jeng), to be published in Proceedings of the Conference on Quantum Electronics and Laser Science, Baltimore, Maryland, 1991.

2. "UV Curable Epoxy-Based Second Order Nonlinear Optical Materials: Synthesis and Characterization," (R.J. Jeng, Y.M. Chen, B.K. Mandal, J. Kumar and S.K. Tripathy), to be published in Electrical, Optical and Magnetic Properties of Organic Solid State Materials, (L.Y. Chiang, A.F. Garito and D.J. Sandman, Eds.) Proceedings of MRS Meeting 247 (1992)..

3. "Dynamic Mechanical Behavior of Photocrosslinkable Nonlinear Optical Polymers," (S. Marturunkakul, J.Y. Lee, S.K. Sengupta, J. Kumar and S.K. Tripathy), to be published in in Electrical, Optical and Magnetic Properties of Organic Solid State Materials, (L.Y. Chiang, A.F. Garito and D.J. Sandman, Eds.) *Proceedings of MRS Meeting* 247 (1992).

4. "Stable Second-Order Optical Nonlinearity in Novel Photocrosslinkable Polymers," (L. Li, X. Zhu, R.J. Jeng, Y.M. Chen, J. Kumar and S. Tripathy), Proceedings of Conference on Emerging Optoelectronic Technologies, SPIE, (S. Selvarajan, Ed.), Tata McGraw-Hill, Bombay, India, 1992.

g. Number of patents granted (list attached): **1**

i. "PhotoCross-Linked Second Order Nonlinear Optical Polymers" (with B.K. Mandal, J.C. Huang and J. Kumar), U.S. Patent No. 5,112,881.

j. Honors/Awards/Prizes for contract/grant employees (list attached): **4**

1. The University of Massachusetts Lowell Graduate Research Scholar Award was awarded to Mr. Lian Li, in 1992, for his outstanding scholarship during his graduate studies at the University of Massachusetts Lowell.

2. The Department of Physics Outstanding Graduate Student Award was awarded to Mr. Lian Li, in 1992, for his outstanding scholarship during his graduate studies at the University of Massachusetts Lowell.

3. The Mark Jonathan Elliot Scholarship Award was awarded to Mr. Ru Jong Jeng, in 1992, for his outstanding scholarship during his graduate studies at the University of Massachusetts Lowell.

4. The Mark Jonathan Elliot Scholarship Award was awarded to Dr. Jun Young Lee, in 1991, for his outstanding scholarship during his graduate studies at the University of Massachusetts Lowell.